

**STANDARD OPERATING PROCEDURE FOR
Polychlorinated Biphenyls (PCBs) FIELD TESTING
FOR SOIL AND SEDIMENT SAMPLES**

The Office of Environmental Measurement and Evaluation
EPA Region New England
11 Technology Dr
North Chelmsford, MA 01863

Prepared by: _____ Date: _____
Scott Clifford, Chemist
Investigations and Analysis Unit, OEME

Approved by: _____ Date: _____
Agnes Van Langenhove, Laboratory QA Officer
Investigations and Analysis Unit, OEME

Approved by: _____ Date: _____
Robert Maxfield, Chief
Investigations and Analysis Unit, OEME Unit Manager

Table of Contents

<u>Section</u>	<u>Subject</u>	<u>Page</u>
1.	Scope and Application	3
2.	Summary of Method	4
3.	Definitions	4
4.	Health and Safety Warnings	5
5.	Cautions	6
6.	Interference	6
7.	Personnel Qualifications	6
8.	Equipment and Supplies	6
9.	Sample Collection	7
10.	Sample Preparation	8
11.	Sample Analyses	9
12.	Qualitation and Quantitation	10
13.	Data and Records Management	10
14.	Quality Control	11
15.	References	12

Figures:

1.	Chromatograms	14
----	---------------------	----

1.0 Scope and Application:

- 1.1 The procedure contained herein is applicable to all EPA Region 1 chemists performing screening for PCBs in sediment or soil samples.
- 1.2 This method is applicable for the screening of soils and sediments for the presence of commercial polychlorinated biphenyl (PCB) mixtures, also known as Aroclors. Chlorinated pesticides can also be done by this method. The following Aroclors can be identified and quantitated by this method.

Table I - Target List

<u>Aroclor</u>	<u>RL ($\mu\text{g/g}$)</u> (ppm)	<u>CAS Number</u>
1016/1242	1	12674-11-2 (1016) 53469-21-9 (1242)
1248	1	12672-29-6
1254	1	11097-69-1
1260	1	11096-82-5#
1262	1	37324-23-5
1268	1	11100-14-4

Notes:

Reporting Limits (RL) are approximate and based on wet weight.

Aroclors 1016 and 1242 may not be distinguishable under some analysis conditions.

Depending on the data quality objectives, it maybe possible to achieve lower RLs by increasing instrument gain, or increasing injection volumes, etc....

- 1.3 Application of this screening method is appropriate for the following quality assurance objectives as outlined in Quality Assurance/Quality Control Guidance for Removal Activities, OSWER Directive 9360.4-01, US EPA, Washington, D.C., April, 1990.
- a) Quick preliminary assessment of site contamination (QA1).
- b) Initial analytical results which are verified by more rigorous methodology on at least 10 % of the samples collected (QA2).
- 1.4 This field testing analytical method provides a means to obtain results in a timely manner. Limitations to the method include target analytes being reported on a wet weight basis and that no second column confirmation is done for the target analytes. It is most useful as a guidance tool for ongoing field work. It is strongly recommended that samples near site action levels, as well as 10 % of the samples, undergo confirmation by traditional analytical procedures such as Method 8080 (SW-846) or Contract Laboratory Program procedures for Pesticide/PCBs as described in SOW OLM04.2, Exhibit D Pesticides/Aroclors.

2.0 **Summary of Method:**

- 2.1 Approximately 1 gram of soil/sediment sample is extracted with a water/methanol/hexane mix in a 4 mL vial. An aliquot of the hexane layer of the extract is analyzed on a gas chromatograph equipped with an electron capture detector (GC/ECD). The typical approximate reporting limit for individual PCBs is 1 µg/g (ppm).
- 2.2 PCB standards at known concentrations are analyzed. Target analytes in samples are tentatively identified and semi-quantitations are made. Identifications are made by comparison of retention times, peak shapes and peak patterns of the sample to the standards. Quantitations are based on sample peak areas or peak heights relative to standard peak areas or peak heights.

3.0 **Definitions:**

- 3.1 FIELD DUPLICATES (FD1 and FD2) -- Two separate samples collected at the same time and place under identical circumstances and treated exactly the same throughout

field and laboratory procedures. Analyses of FD1 and FD2 give a measure of the precision associated with sample collection, preservation, and storage, as well as with laboratory procedures.

- 3.2 LABORATORY REAGENT BLANK (LRB) -- The reagents are treated exactly as a sample including exposure to all glassware and equipment that is used with the other samples. The LRB is used to determine if method analytes or other interferences are present in the laboratory environment, the reagents, or the apparatus.
- 3.3 STOCK STANDARD SOLUTION -- A concentrated solution containing one or more method analytes prepared in the laboratory using assayed reference materials or purchased from a reputable commercial source.
- 3.4 WORKING STANDARD SOLUTION -- A solution of several analytes prepared in the laboratory from stock standard solutions and diluted as needed to prepare calibration solutions and other needed analyte solutions.
- 3.5 **PROFICIENCY TESTING (PT)/PERFORMANCE EVALUATION SAMPLE (PES):**
A sample, the composition of which is unknown to the laboratory or analyst, provided to the analyst or laboratory to assess the capability to produce results within acceptable criteria. This is optional depending on the data quality objectives.
- 4.0 **Health and Safety Warnings:**
 - 4.1 The toxicity or carcinogenicity of each reagent used in this method has not been precisely determined; however, each chemical should be treated as a potential health hazard. Exposure to these reagents should be reduced to the lowest possible level. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of data handling sheets should be made available to all personnel involved in these analyses.
 - 4.2 Always wear safety glasses or a shield for eye protection, protective clothing, and observe proper mixing when working with these reagents.
 - 4.3 Some method analytes have been tentatively classified as known or suspected human or mammalian carcinogens. Pure standard materials and stock standard solutions of these compounds should be handled with suitable protection to skin, eyes, etc.

5.0 Cautions:

- 5.1 The working standard is replaced every 12 months.

6.0 Interferences:

- 6.1 Method interferences may be caused by contaminants in solvents, reagents, glassware and other sample processing hardware that lead to discrete artifacts and/or elevated baselines in the chromatograms. All of these materials must routinely be demonstrated to be free from interferences under the conditions of the analysis by running a LRB.
- 6.2 Matrix interferences may be caused by contaminants that coelute with the target compounds. The extent of matrix interferences will vary considerably from source to source. An acid clean up may eliminate this interference.
- 6.3 Contamination by carry-over can occur whenever high level and low level samples are sequentially analyzed. To reduce carry-over, a LRB should be analyzed following an unusually concentrated sample to assure that the syringe is clean. Alternatively, an injection of clean solvent (hexane) can be used to assess potential carry-over.

7.0 Personnel Qualifications:

- 7.1 The analyst should have at least a four year degree in a physical science.
- 7.2 The analyst should be trained at least one week and have a working knowledge of this method and quality control before initiating the procedure.
- 7.3 All personnel shall be responsible for complying with all quality assurance/quality control requirements that pertain to their organizational/technical function.

8.0 Equipment and Supplies:

- 8.1 Sample collection containers: 4 - 8 oz glass jars or plastic bags with zippered

seals. (Plastic bags are preferred.)

- 8.2 Sample preparation containers: 4 mL glass vials with screw cap and teflon septum.
- 8.3 Stainless steel spatula.
- 8.4 Micro syringes: 10 - 1000 μ L with chromatographic syringes.
- 8.5 Top-loading balance capable of weighing to the nearest 0.01 g.
- 8.6 Gas chromatograph equipped with an electron capture detector and all required accessories, including GC column, recorder, and nitrogen carrier gas.
- 8.7 GC Column: 30 m, 0.53 mm megabore capillary column, DBPS-5 or equivalent column
- 8.8 Hexane - Pesticide residue analysis grade or equivalent
- 8.9 Methanol - Pesticide residue analysis grade or equivalent
- 8.10 Reagent Water - free of all interfering contaminants
- 8.11 Standard Stock Solutions - Calibration standards made from pure standard materials or purchased as certified solutions.
- 8.12 Working Calibration Standard - The working calibration standard concentrations should be 1.0 μ g/mL, measured to two significant figures.
- 8.13 PE Check Sample - Solid matrix QC check standard purchased from a commercial vendor/supplier. Accompanying documentation must include true value and acceptance limits.
- 8.14 Sulfuric Acid Solution - 1:1 (v/v) Sulfuric Acid (optional)

9.0 **Sample Collection:**

- 9.1 Place approximately 20-50 g of soil/sediment into sample collection container.

9.2 It may be appropriate to decant liquid from some samples.

10.0 Sample Preparation:

10.1 Mix sample thoroughly in container. Avoiding twigs and small pebbles weigh approximately 1 gram of sample into a 4 mL vial. Record the weight wet to the nearest 0.01 g.

10.2 Add the following solvents to the sample using a 1000 μ L graduated syringe and cap the vial.

200 μ L water
800 μ L methanol
1000 μ L hexane

10.3 Agitate sample for one minute using a vortex mixer. Centrifuge the sample.

10.4 If no dilution or cleanup is required, a 2 μ L aliquot of the hexane layer (top layer) is ready for injection on the GC/ECD.

10.5 Dilutions are made by placing an aliquot of the hexane layer, measured by analytical syringe, into a 2 mL crimp-top vial. The appropriate amount of hexane is added quantitatively, using an analytical syringe.

10.6 Prepare a LRB and QC check sample, using clean sand and a solid matrix QC sample, and following steps 10.2 to 10.3.

10.7 (Optional) Acid cleaning is an effective way to remove some method interferences without alteration of the target PCBs. To acid clean the sample, separate the hexane layer from the water/methanol layer and add it to a clean 4 mL vial. Add 1 mL of 1:1 (v/v) sulfuric acid. Seal the vial tightly; sulfuric acid can damage skin and clothing. Agitate the sample for one minute by vigorous manual shaking or vibration. Remove the hexane layer. A 2 μ L aliquot of the hexane layer is analyzed by GC/ECD.

11.0 Sample Analysis:

- 11.1 Prepare calibration standards for all PCBs of interest. If the PCB type is unknown, Aroclors 1242, 1254, and 1260 are used to characterize the site.
- 11.2 Allow the GC carrier gas flow and the oven temperature to equilibrate. The oven temperature should be set at approximately 200°C. Analyze the target PCB standard or each of the calibration standards (1242, 1254, 1260) with a 2 µL injection volume. Calibration standards are at approximately 1.0 µg/mL and must be measured to two significant figures. Carrier gas flows must be adjusted to achieve PCB patterns that are unique to each PCB of interest.
- 11.3 Repeat the injection of the target PCB standard(s) for reproducibility. The peak heights should be within $\pm 15\%$ of each other with identical retention times.
- 11.4 Once GC analytical conditions are established for the standards, the QC check sample, LRB, and samples must be analyzed under the exact same conditions.
- 11.5 Inject 2 µL of the QC sample. The acceptance criteria is within the manufacturer's accepted range.
- 11.6 Inject 2 µL of the LRB before any sample analyses. The method blank must not contain any peaks which fall within the retention time of any of the peaks of the PCBs of interest. **Acceptance criteria: No interfering peaks greater than one-half the reporting level.**
- 11.7 Inject the samples using a 2 µL injection volume. All GC operating conditions must be the same as those established for the calibration standards. The attenuation is adjusted so the signal remains on scale, otherwise a dilution is used.
- 11.8 Carryover may occur from highly concentrated samples. Minimize carryover by the thorough flushing of the injection syringe with hexane between analyses. Also, all syringes used for sample dilutions must be thoroughly flushed to minimize carryover. Additional method blank analyses may be required to demonstrate the absence of carryover.
- 11.9 Continuing Calibration standards for PCBs of interest must be analyzed at least once every 10 samples and at the end of the batch. More frequent standardization may be required to accommodate instrument variations. The standard should be

within $\pm 20\%$ of each other and identical retention times.

12.0 Qualitation and Quantitation:

- 12.1 Tentative identifications of PCBs are made by comparison of sample peak patterns and retention times against PCB standard peak patterns and retention times. Figure 1 has examples for some of the target PCBs.
- 12.2 Quantitation of PCBs is performed by the external standard method. The peak height of a representative peak in the sample is compared to the peak height of the same peak in the PCB standard analyzed closest in time to the sample. The injected concentration is determined by a direct ratio with the standard. The final concentration is corrected for sample size.

Concentration in extract ($\mu\text{g/mL}$)

$$\text{Conc. } (\mu\text{g/g}) = \frac{\text{Std conc.}(\mu\text{g/mL}) * \text{Sample's peak height} * 1 \text{ mL} * \text{Dil}}{\text{Std peak height} * \text{Wet Weight (g)}}$$

Example:

A 0.90 gram sample is extracted into 1 mL of hexane. The PCB is determined to be 1254 by qualitative evaluation. A 2 μL injection of the 1254 standard at 1.0 $\mu\text{g/mL}$ analyzed closest to the sample results in a peak at 3.0 min with a peak height of 75 mm. A 2 μL injection of the sample has a peak at 3.0 min with a peak height of 30 mm. The following calculation is used to determine the final concentration.

$$\text{Conc. } (\mu\text{g/g}) = \frac{1.0 \mu\text{g/mL} * 30 \text{ mm} * 1 \text{ mL} * 1}{75 \text{ mm} * 0.90 \text{ g}} = 0.44 \mu\text{g/g}$$

13.0 Data and Records Management:

- 13.1 All work performed for the analyses of samples should be entered into the field screening logbook. The analyses data should be presented to the project manager on site. This is followed up by an Internal Correspondence Report, that is reviewed by the Advanced Analytical Chemistry Expert from the Chemistry

Section of the EIA Laboratory. Chromatograms generated should be saved and filed in the project folder. The samples analyzed should also be logged into the laboratory tracking system.

13.2 Chromatograms:

13.2.1 Site name, analyst name, and date at the start of the chromatogram strip chart.

13.2.2 Every chromatogram/every sample/standard

Sample number or standard
Volume injected
Attenuation setting
Dilutions

14.0 **Quality Control:**

14.1 A blank and a one point standard for each target Aroclor is used for instrument calibration. Initially run one PCB standard to determine retention times and response factors of instrument. Repeat a second standard to check the reproducibility. **Acceptance criteria: within $\pm 15\%$ difference from the first standard.**

14.2 Blanks are analyzed at the initial calibration and periodically to be sure of no carry over from previous injections. Technical judgement is used to determine frequency. **Acceptance criteria: No interfering peaks greater than one-half the reporting level.**

14.3 An external quality control sample is analyzed with every daily batch of samples. This is a soil matrix. **The acceptance criteria is the observed value within the manufacturer's acceptance range.**

14.4 A continuing calibration standard is run at least every 10 samples and at the end of the sample batch to update the instrument's calibration. **Acceptance criteria: $\pm 20\% \Delta$ agreement with the previous calibration.**

14.5 Run field and laboratory duplicates at 5% frequency. **Acceptance criteria: RPD $\pm 30\%$.**

- 14.6 When possible, GC confirmation of 10% of the field samples analyzed should be performed using RCRA 8082 or CLP OLM04.2. This is done, dependent upon the project data quality objective.

15.0 **References:**

- 15.1 Interim Final Guidance for the Quality Assurance/Quality Control Guidance for Removal Activities, April 1990.

Quality Control Table			
QC Item	Frequency	Acceptance Criteria	Corrective Action
Initial Calibration	Daily, before samples	< 15%D, done ¹ visually for some stds	Inject another std, check system
Cont. Cal	Every 10 samples and at the end of sample batch	< 20%RPD, ¹ done visually for some stds	Inject another std, repeat initial calibration, check system, rerun samples if necessary
PES/QC Sample	Daily, every batch	Within the ¹ manufacturer's accepted range	Repeat injection, repeat another QC, run new std, check system
LRB	Daily, every batch	< 1/2 RL ¹	Repeat blank injection, prepare a new blank, check system, increase RLs depending on the DQOs
Field Duplicate	Option, depends on DQOs	< 30% RPD ¹	Repeat injection, run another duplicate
Laboratory Duplicate	5% frequency	< 30% RPD ¹	Repeat injection, run another duplicate

¹= Acceptance criteria defined based on technical judgment

Figure 1: Examples of Typical Aroclors

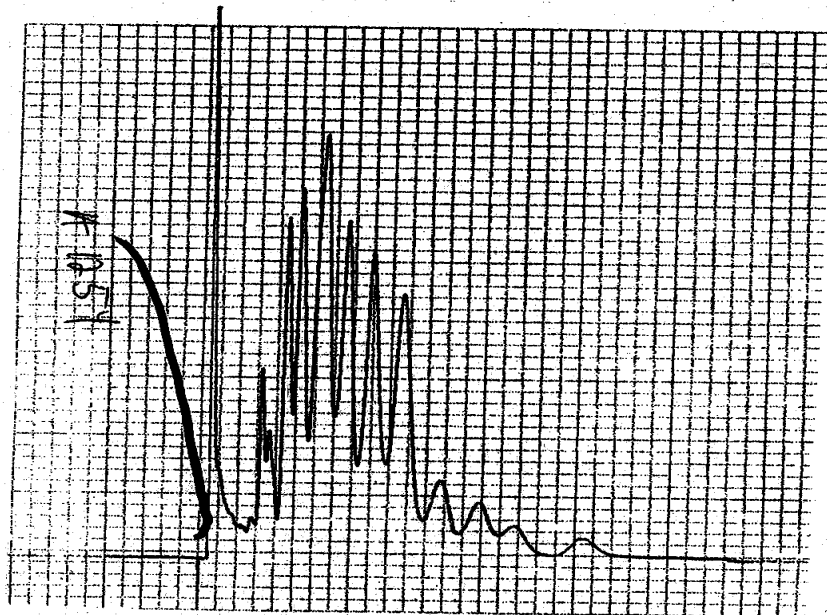
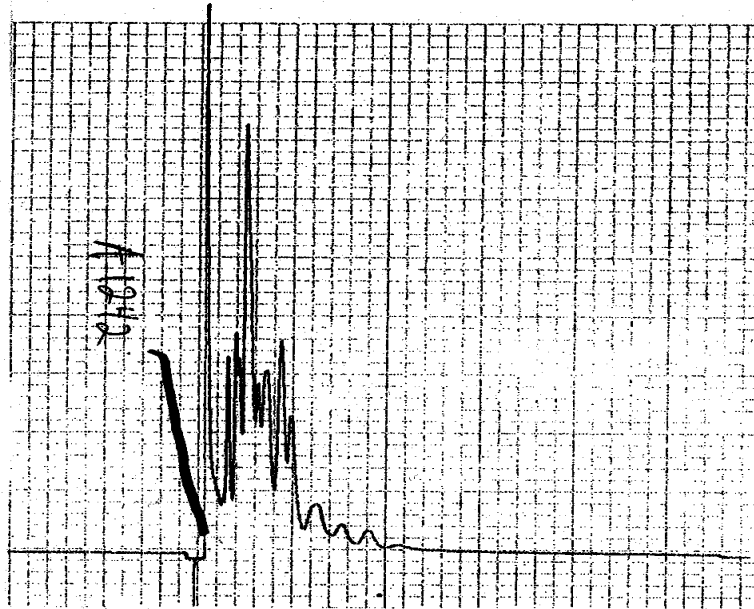


Figure 1: Examples of Typical Aroclors

